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# Na order and Co charge disproportionation in $Na_xCoO_2$

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ABSTRACT

We have synthesized and characterized different stable phases of sodium cobaltates $Na_xCoO_2$ with sodium content $0.65 < x < 0.80$. We demonstrate that $^{23}Na$ NMR allows us to determine the difference in the susceptibility of the phases and reveals the presence of Na order in each phase. $^{59}Co$ NMR experiments give clear evidence that Co charge disproportionation is a dominant feature of Na cobaltates. Only a small fraction ( $\approx 25\%$) of cobalt are in a non-magnetic $Co^{3+}$ charge state whereas electrons delocalize on the other cobalt. The magnetic and charge properties of the different Co sites are highly correlated with each other as their magnetic shift $K_{ZZ}$ scales linearly with their quadrupolar frequency $\nu_Q$. This reflects the fact that the hole content on the Co orbitals varies from site to site. The unusual charge differentiation found in this system calls for better theoretical understanding of the incidence of the Na atomic order on the electronic structures of these compounds.



## 1. Introduction

The influence of the dopant atoms on the electronic properties of conducting layers has initiated large debates in High Temperature Superconducting (HTSC) cuprates as well as in other complex layered oxides of transition elements. Whereas in many systems this influence is masked by miscellaneous effects, there are many experimental evidences that in the sodium cobaltates $Na_xCoO_2$ a large interplay between the Na atomic ordering and the electronic density on the Co sites occurs.

As HTSC cuprates the sodium cobaltates $Na_xCoO_2$ are layered oxide materials and the charge doping of the $CoO_2$ layers is controlled on a large range by variation of the Na content. This can be put in parallel with the doping of the cuprates by chemical substitutions on the layers separating the $CuO_2$ planes. One significant difference with the cuprates is that the Co of the $CoO_2$ plane are ordered on a triangular lattice and not on a square lattice as for the $CuO_2$ plane of the cuprates. In this configuration the large crystal field on the Co site favors a low spin state [1] in which orbital degeneracy influences significantly the electronic properties and may yield large thermoelectric effects [2]. A rich variety of other physical properties ranging from ordered magnetic states [3], high Curie–Weiss magnetism and metal insulator transition [4], superconductivity [5], etc. have then been observed on the cobaltates. These differences with the cuprates have apparently recently stimulated an increased interest of theorists as monitored by recent publications [6–8].

In sodium cobaltates the low spin configuration for the Co ions should correspond to $3^+$ or $4^+$ charged states with spin $S=0$ and $S=1/2$ respectively. Many experiments and theoretical calculations have considered that the Co magnetism either is uniform or that there is a $Co^{3+}/Co^{4+}$ charge segregation with localized magnetic moments. However it has been evidenced by NMR by many groups that for $x \geq 1/2$ the $Na^+$ displays an atomic ordering associated with Co charge disproportionation and itinerant magnetism in the planes [9–16]. Na ordered atomic structures have been observed in sodium cobaltates by TEM [17], neutrons [18], and x-rays [19–21]. However, the experimental situation that prevails so far is quite unusual in solid state physics, as most experiments do not permit altogether to establish reliably the relation between the local order proposed, the actual Na content and the local magnetic properties of the studied samples.

On the contrary $^{23}Na$ and $^{59}Co$ NMR experiments have proved to be excellent probes allowing to evidence not only the Na atomic order but also that Co charge disproportionation occurs. In this paper we summarize our NMR study of sodium cobaltates $Na_xCoO_2$ with sodium content $0.65 < x < 0.80$ which allowed us to establish this correlation for the specific $x = 2/3$ [22,20,16] and $x=0.77$ phases [23–25]. We also compare the properties of the studied phases with properties of the $x=1$ and $x = 1/2$ compounds.

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